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CONTENTS

Corrigendum Slip for Section A, Part II, Vol. 16, 1947

Errata

Read	positively	for	pcsitively	line	6, page 37
,,	tl oroughly	,,	throughly	,,	12, page 39
,,	an	,,	on	,,	26, page 39
,,	colloidal	,,	solloidal	,,	14, page 41
,,	unipolar	,,	unipɔlar	,,	7, para 2, page 45
,,	ɼotential	,,	pɔtential	,,	13, page 47
,,	$\overline{2}\cdot9044$	,,	$2\cdot\overline{9}044$	,,	1, table 1, page 48
,,	$\overline{13}\cdot7294$	,,	$13\cdot7294$	,,	1, table 1, page 48

STUDY OF THE PREPARATION AND PROPERTIES OF ARGENTOTHIOSULPHATE COMPLEXES AND DETERMINATION OF THE VALENCY OF THE COMPLEX RADICAL BY COAGULATION EXPERIMENTS.

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ABSTRACT

Different samples of sodium argentothiosulphate have been prepared by alcoholic precipitation from a solution of silver halide (chloride or bromide) in a concentrated solution of sodium thiosulphate. The various properties of the isolated products have been studied. The results of analysis of the product gave the composition as : $Ag_2S_2O_3, 4Na_2S_2O_3, 2H_2O$, for all the samples. The valency of the complex ion was determined by coagulation of a positively charged ferric oxide sol with standard solution of the complex compound and by comparing the coagulation values with those for electrolytes of known valencies. The values showed that the complex radical was bivalent in character. On a systematic study of the formation of complex argento-thiosulphates it has been concluded in an earlier communication, that only mono- and tri-valent complex anions are capable of existence in a solution of silver halide in sodium thiosulphate. On the other hand quantitative analysis leads to a formula which does not correspond with any of those already arrived at. The isolated product contains a much larger proportion of thiosulphate and it is therefore evident that the bivalency of the predominant ion thiosulphate is responsible for the abnormal coagulation values for the complex ion. It has been emphasized that in order to obtain a true formula of any co-ordination compound physico-chemical methods must be adopted as the formula obtained by isolation and subsequent analysis always include those of double salts and absorption complexes as well.

A 47-2-1

INTRODUCTION

It is well known that the removal of silver halide by sodium thiosulphate solution during fixation of photographic negatives involves the formation of complex compounds. The investigations of argentothiosulphates have been of considerable interest and compounds of different compositions have been isolated from the solution by various workers. Mention may be made of the work of Baines[1], and Spacu Murgulescu[2] who analysed some samples and assigned formulae to the products. In an important communication[3] Basset and Lemon described the examination of the system $Na_2S_2O_3$ — $Ag_2S_2O_3$ — H_2O, at 25° and concluded the formation of the following complex compounds :

(i) $Na_3[Ag(S_2O_3)_2], H_2O$ or $3Na_2S_2O_3 . Ag_2S_2O_3 . 2H_2O$

(ii) $Na_5[Ag_3(S_2O_3)_4], 2H_2O$ or $5Na_2S_2O_3 . 3Ag_2S_2O_3 . 4H_2O$

(iii) $Na[Ag(S_2O_3)], H_2O$ or $Na_2S_2O_3 . Ag_2S_2O_3 . 2H_2O$

(iv) $Na[Ag_3(S_2O_3)_2], H_2O$ or $Na_2S_2O_3 . 3Ag_2S_2O_3 . 2H_2O$

The divergent results recorded in literature led us to investigate the formation of argentothiosulphate complexes and in a recent paper[4] we described our results on the compositions of such compounds studied by the solubility method[5] devolved by us, for elucidation of the formulae of complex compounds.

In this paper we have described the preparation and properties of sodium argentothiosulphate obtained by alcoholic precipitation from a solution of silver halide (chloride or bromide) in a concentrated solution of sodium thiosulphate. The chemical composition has also been determined by quantitative analysis. Incidentally an attempt was made to determine the valency of the complex ion by the coagulation of a colloidal solution of positively charged ferric oxide, a method similar to that adopted by Ghosh and Dhar[6] for showing the bivalency the fluorideion.

EXPERIMENTAL.

Preparation :—20 grams of 'AnalaR' silver nitrate was dissolved in water and silver halide was precipitated by the addition of either

'AnalaR' hydrochloric acid solution or a solution of chemically pure sodium bromide. The precipitated silver halide was thoroughly washed free from the precipitating electrolytes and then dissolved in a concentrated solution of sodium thiosulphate of 'AnalaR' quality, care being taken to use the minimum quantity of sodium thiosulphate. To the solution was added about 150 c.c. of absolute alcohol and the heterogeneous mixture shaken vigorously when a white emulsion appeared and later an oily liquid separated at the bottom of the vessel. This oily liquid was separated by means of a separating funnel and received in an evaporating dish to which was then added a further quantity of alcohol. On stirring with a glass rod, a white solid mass separated out. The lumps were broken and washed throughly with alcohol and dried at a room temperature of about 30°. It was found that the compositions of different samples, whether prepared from silver chloride or silver bromide, were the same and the properties were also similar.

Properties : —The product has a colourless appearance and is fairly soluble in water. Hydrochloric acid separates sulphur from the compound, with brisk evolution of sulphur dioxide while silver chloride does not separate out. Nitric acid behaves in the same way as hydrochloric acid, and on boiling a clear solution is obtained.

The compound is readily soluble in ammonium hydroxide, and on adding nitric acid to the ammoniacal solution, some white particles separate out which change through a series of colours' and finally become black. This is probably due to the formation of silver sulphide from the complex. When on aqueous solution is reacted with silver nitrate, silver in the complex gets perecipitated first as thiosulphate and finally changes to silver sulphide.

The compound does not fuse on heating, but burns with a bluish flame and a black residue is left. The compound does not darken on exposure to sunlight but an aqueous solution when exposed to solar light for six hours assumed a sky blue tinge. Darkening of the solid occurs with time and it becomes dark grey in a period of about six

months. Similarly an aqueous solution, when kept for four months deposited silver mirror on the vessel.

The compound responds to the tests for thiosulphate, but the tests for silver are not obtained.

Analysis :—The analysis was carried out as described in the following lines ; Silver, thiosulphate and water of crystallisation were determined, while sodium was found by difference. The methods of analysis are given below.

Silver :—0.4 gram of the compound was weighed accurately and boiled vigorously with nitric acid to decompose the complex and thus a solution of silver nitrate was obtained. Silver was precipitated from the solution as chloride and estimated as usual.

Thiosulphate :—Thiosulphate was estimated by the method recently described by us[7]. 0.5 gram of the compound was accurately weighed dissolved in water and a solution of silver nitrate was added to it drop by drop with occasional stirring till precipitation was complete . The precipitate which was originally white gradually changed to yellow, red and finally became black, due to the conversion of silver thiosulphate to silver sulphide. The precipitate was filtered in a Gooch crucible, washed with water and the filtrate was concentrated to a volume of about 200 c.c. From the filtrate barium sulphate was precipitated by the addition of barium nitrate, and sulphate estimated. The Gooch crucible containing the silver sulphide precipitate was dried in an oven at 120^0, till constant weight was attained. The total amount of sulphur contained in the complex was calculated from the weights of barium sulphate and silver sulphide :

$$\text{Total sulphur} = \text{Weight of silver sulphide} \times 0.12937$$
$$+ \text{Weight of barium sulphate} \times 0.13738$$

From the weight of sulphur the amount of oxygen in $S_2O_3^{--}$ was calculated.

Water of crystallisation :—1 gram of the compound was taken in a watch glass, and heated to a constant weight in an air oven at 120^0. The loss in weight gave the amount of water of crystallisation.

The average composition of the compound, arrived at by the analysis of a number of samples is given in table I.

TABLE I

	Found	Calculated
Silver	21.46%	21.69%
Sulphur	32.10%	32.13%
Oxygen (Calculated from the amount of sulphur)	24.08%	24.10%
Sodium (by difference) ...	18.66%	18.46%
Water of crystallisation ...	3.70%	3.62%
	100.00%	100.00%

Formula : $Ag_2S_2O_3$. $4Na_2S_2O_3, 2H_2O$.

Coagulation experiments:—The determination of valency by the coagulation of solloidal solutions was first suggested by Freundlich,[8] and applied to show the bivalent nature of the fluoride ion by Ghosh and Dhar[6]. In this study a colloidal solution of positively charged ferric oxide was prepared by dispersing freshly precipitated hydrated ferric oxide by acetic acid, and purifying as usual by dialysis. The amount of ferric oxide in the sol was estimated by evaporating a measured volume to dryness, and finally heating strongly to a constant weight.

Concentration of the sol = 7.69 grams Fe_2O_3 per litre

For determining the coagulation values different amounts of the sol were taken in clean test tubes, and measured volumes of electrolytes were added. The time of observation was half an hour. The experiments were conducted at 25° and the total volumes were kept 10 c.c. in every case.

Coagulation with electrolytes

TABLE II

Volume of electrolyte required

Volume of sol	M/5 KCl	M/400 K_2SO_4	M/1500 $K_3Fe(CN)_6$	M/2000 $K_4Fe(CN)_6$
1 c.c.	2.1 c.c.	0.5 c.c.	0.5 c.c.	0.4 c.c.
2 c.c.	2.8 c.c.	1.0 c.c.	1.0 c.c.	0.8 c.c.
3 c.c.	3.4 c.c.	1.4 c.c.	1.5 c.c.	1.2 c.c.

Coagulation with the complexes

TABLE III

Volume of sol	Volume of M/500 solutions of the complexes	
	Complex (1) from AgCl	Complex (2) from AgBr
1 c.c.	0.45 c.c.	0.40 c.c.
2 c.c.	0.80 c.c.	0.80 c.c.
3 c.c.	1.25 c.c.	1.20 c.c.

From the above results we find that the coagulative power of the various electrolytes lie in the following order :

$K_4Fe(CN)_6 > K_3Fe(CN)_6 >$ Complex (1) — Complex (2) $> K_2SO_4 >$ KCl
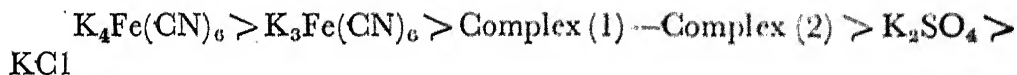
The coagulation values due to the complex ion lie near that of sulphate ion, thus showing the bivalency of the complex.

DISCUSSION

It has already been said that a number of molecular compounds have been isolated from a solution of silver halide in sodium thiosulphate. Our results on the composition of these complexes (*loc. cit*) have conclusively proved that only two complex anions, viz., $[Ag(S_2O_3)]^-$ and $[Ag(S_2O_3)_2]^{-3}$ are capable of existence, their formation depending on the concentration of sodium thiosulphate solution used. With a concentrated solution of thiosulphate the reaction is :

$$AgX + Na_2S_2O_3 \rightleftharpoons Na[Ag(S_2O_3)]$$
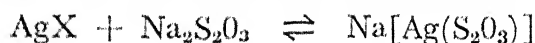
when however, the thiosulphate concentration is lower, complex formation takes place according to the equation :

$$AgX + 2Na_2S_2O_3 \rightleftharpoons Na_3[Ag(S_2O_3)_2]$$
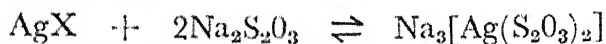
The compound $Na[Ag(S_2O_3)]$ was prepared by workers including Richards and Faber[9], Rosenheim and coworkers[10] and Baines (*loc. cit*), whereas $Na_3[Ag(S_2O_3)_2]$ was prepared, in comparatively recent years, by Spacu and Murgulescu (*loc. cit*). The other compounds reported by Basset and Lemon (*loc. cit*) seem to be double compounds or adsorption complexes, incorporating the two complexes with indefinite amounts of thiosulphate associated.

Our results described in this paper lead us to the formula : $Ag_2S_2O_3, 4Na_2S_2O_3, 2H_2O$, for the isolated product. On the other hand from the solubility results it is evident that the compound in presence of a higher concentration of thiosulphate should have been $Na[AgS_2O_3]$. It appears, therefore, that the isolated compound is an adsorption complex or a double salt. If the isolated compound would have been a true complex, the valency of the complex anion should have a value far greater than 4, The charge on the complex radical and thence its valency was determined by coagulation of a positively charged ferric oxide sol. The results indicate that the complex anion is bivalent, thus suggesting that this coagulation value is mainly due to the thiosulphate ion which is present in large excess, as a double salt or adsorption compound. It seems that some of the compounds isolated by Baines also belong to this type of compounds.

It should, therefore, be remembered that results obtained by methods of isolation and subsequent analysis are generally not very reliable, as they always include in their composition those of adsorption complexes and double salts as well. These complications are liable to mask the clear composition of the true co-ordination compounds formed. It is thus absolutely necessary that in addition to usual analysis physico-chemical methods must be adopted in order to elucidate the exact compositions of the complexes that may be formed.

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THERMAL IONIZATION OF CALCIUM AND DETERMINATION OF SPECIFIC CHARGE OF Ca+.

By

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ABSTRACT

The thermal ionization of calcium has been studied using the vacuum graphite furnace constructed by Saha and Tandon. The specific charge of Ca+ has been determined by applying the space charge theory to positive currents under various potentials as explained in the paper on Lithium. The contribution of the terms $b(T)$ and $b'(T)$ for Calcium in the ionization formula tends to lower the effective ionization potential. The mean value of the energy of ionization is 136·9 K. cals. The value of the specific charge of calcium is 7.5×10^{12} e. s. u./gm.

1. INTRODUCTION.

The Space charge theory for unipolar currents was developed by Srivastava and Bhatnagar (1944 a), and was applied by them (Srivastava and Bhatnagar, 1944 b) to determine the e/m for electrons from graphite. In a subsequent paper (Srivastava and Bhatnagar 1946) the theory was applied to determine the specific charge of Li+ using a strong magnetic field to deflect off the electrons and obtaining thereby, an effectively unipolar positive current; the e/m for the positive particle is then obtained from the relation giving the variation of the positive current with voltage applied to the Faraday cylinder.

In the present paper the same method has been employed to determine the specific charge of Ca+. A study of the thermal ionization of Calcium has also been made, the elements barium and strontium of the same group, having been studied by Srivastava (1940 a 1940 b).

A 47-2-2

2. Thermal Ionization of Calcium.

A detailed description of the apparatus and the experimental procedure has been given by Srivastava in his paper on strontium. (Srivastava 1940 b).

Due to high ionization potential of calcium (6.02 eV) the temperatures at which measurable ionization could be produced in the graphite furnace was higher than hitherto employed in similar experiments. The side-furnace which contains the metal was modified to develop a temperature at which calcium has enough vapour pressure to produce appreciable ionization. Existing data on the vapour pressure of calcium show that, in the region of the temperature range at which the present measurements have been made, values of the vapour pressure of calcium are not available. The following procedure had, therefore, to be adopted to get the values of the vapour pressure at the different temperatures used in the experiments.

There are two sets of data available, one for solid state given by Rudberg (1934) and the other for liquid state by Ruff and Hartmann (1924) The data on the solid state are at lower and those on the liquid state are at higher temperatures than those in our experiment. Therefore, to get the values of vapour pressure for our range of temperature the solid state data have been extrapolated to the melting point of calcium, and similarly, the data on the liquid state have been extrapolated downwards to the melting point. The difference between the slopes of the curves so obtained agrees well with the latent heat of fusion of calcium (cf. Srivastava's paper on strontium) and shows that the values of the vapour pressure for higher temperatures, as read from the vapour pressure curve for solid state by extrapolating it to the melting point can be taken as correct. As a further check the value of the vapour presure has also been calculated from the formula

$$log\, p(\text{mm}) = -\frac{9670}{T} + 8.15,$$

as given by Rudberg.

The calculated values agree well with those obtained by graphical extrapolation. A mean of these two values has been utilized to

get the vapour pressure in the side tube containing calcium. Knowing the value of the vapour pressure p' in the side tube at temperature T', the value of vapour pressure p at temperature T in the main furnace is calculated from the ralation

$$p/p' = \sqrt{T/T'}.$$

Like barium and strontium, for calcium also the contribution of the terms $b\,T$ and $b'\,T$ occurring in the ionization formula

$$\log K = \log \frac{p_i \cdot p_e}{p_a} = -\frac{U}{4.573\,T} + \frac{5}{2} \log T - 6.479 + \log 2$$
$$+ \log b'(T) - \log b(T) \quad \ldots \quad (1)$$

(where the pressures are expressed in atmospheres) is such that it tends to lower the effective energy of ionization—a fact which accounts for the occurrence of calcium in a highly ionized degree in the sun, whereas other elements, with much lower ionization potential, are much less ionized. The values for the case of calcium as calculated from the energy states given by Bacher and Goudsmidt, are

$$b(T) = 1.00029 \text{ at } 2063^\circ \text{ K}$$
$$b'(T) = 2.00097 \text{ at } 2063^\circ \text{ K.}$$

Thus throughout the temperature range of our experiment we can assume $b(T) = 1.00$ and $b'(T) = 2.00$ and the ionization formula (1) becomes

$$\log K = -\frac{U}{4.573\,T} + \frac{5}{2} \log T - 6.479 + 2 \log 2 \qquad . \quad (2)$$

and K from the theory of the experiment is given by (see Srivastava 1940a)

$$K = \frac{2\pi kT}{e^2 S^2} \left(\frac{r^2 + d^2}{r^2} \right)^2 \frac{i_g^+ \cdot i_g^-}{p_a} \cdot \frac{\sqrt{m_i \times m_e}}{(1.013 \times 10^6)^2}, \qquad \ldots \quad (3)$$

where $r =$ the radius of the aperture in limiting diaphragm,

$d =$ distance between the diaphragm and the effusion hole,

$S =$ area of the effusion hole

i_g^- and i_g^+ are the negative and positive currents respectively, and all other quantities have their usual significance.

The values of the currents i_g^- and i_g^+ occurring in the table are the zero-field values of the current obtained, as explained in the paper on thermionic work fuction of graphite (Bhatnagar 1944).

Table I gives the results on the thermal ionization of calcium in the temperature range 1898°K to 2063°K. The mean value for the energy of ionization comes out to be 136.9 K cals which agrees with the spectroscopically determined value 139 K cals within limits of experimental error.

TABLE I

Diameter of effusion hole   ...   .   = 1.008 mm.
Distance between effusion hole and diaphragm = 14.5 mm.
Sensitivity of the galvanometer   ...   ...   = 1.25 × 10⁻⁹ amp/mm
Radius of limiting diaphr. gm aperture   = 4.2 mm.

Mean Temp. of the graphite furnace. °K	Temp. of aux. furnace °K	log p_{ca} (mm.) in aux. fur.	log p_{ca} (mm.) in main fur.	i_g^- mm.	i_g^+ mm.	log k (atmos.)	l in K Cals.
2063	1037	$\bar{2}.755$	2.9044	156 × 100	53	$\bar{13}.7294$	138.7
1973	1047	$\bar{2}.913$	$\bar{2}.9833$	72 × 100	34	$\bar{13}.1023$	137.7
1960	1047	$\bar{2}.913$	$\bar{2}.9833$	80 × 100	30	$\bar{13}.0933$	137.6
1955	1047	$\bar{2}.913$	$\bar{2}.9827$	80 × 100	33	$\bar{13}.1342$	136.8
1949	1047	$\bar{2}.913$	$\bar{2}.9820$	80 × 100	24	$\bar{14}.9952$	137.7
1942	1022	$\bar{2}.630$	$\bar{2}.7705$	80 × 100	27	$\bar{13}.2563$	134.6
1931	1027	$\bar{2}.675$	$\bar{2}.8132$	80 × 100	30	$\bar{13}.2569$	133.9
1917	1027	$\bar{2}.675$	$\bar{2}.8117$	106 × 30	15	$\bar{14}.5536$	139.1
1896	1002	$\bar{2}.440$	$\bar{2}.5797$	41 × 30	11	$\bar{14}.7566$	135.7
1828	982	$\bar{2}.255$	$\bar{2}.3899$	58 × 30	2	$\bar{15}.8155$	137.6

2. DETERMINATION OF *e/m*

It has already been explained in our paper on the space charge effect that the specific charge of the particle carrying the current can be determined by applying the Space Charge theory provided the current is unipolar. This condition is experimentally realised by deflecting, with the help of a strong electromagnet, the electrons from the beam of the charged particles effusing out of the tiny hole in the graphite furnace and, thus preventing them from entering the inter-electrode space which, in our case, is formed by the diaphragm and the Faraday cylinder. The heavy ions (Ca^+) are little affected by the magnetic field and pass through the limiting diaphragm, and are collected by the Faraday cylinder to which a suitable negative potential is applied. The current produced by the charged particles is measured at various potentials on the Faraday cylinder. Table II gives a typical set of observations.

The relation between the current and the applied voltage on taking space charge effect into account is (Srivastava 1946)

TABLE II

V in Volts	d^+ in mm
0.5	3·5
1	4·5
1.2	5
1.5	6
1.8	6·5
2	7
2.5	8
3	9
4	12
5	13·5

$T = 1793°$, $x = 2.1$ cm., $A = \pi \times (.42)^2$, Gal. sens. $= 1.25 \times 10^{-9}$ amp/mm.

$$i \quad = \frac{V^2}{9\pi}\left(\frac{e}{m}\right)^{\frac{1}{2}} \frac{V^{3/2} \times A}{x^2} \quad \text{approx.} \tag{4}$$

where x = distance between the diaphragm and the Faraday cylinder
A = area of the aperture in the diaphragm.

Plotting i against V (see Fig. 1) e/m for the Ca$^+$ ion can be obtained from the slope of the curve. The value so obtained is $e/m = 7.5 \times 10^{12}$ e.s.u/gm which agrees very closely with the calculated value for calcium taking for e the value of electronic charge and for m the mass of Ca atom.

This also identifies the particle producing positive currents in the experiments on the thermal ionization of calcium with Ca$^+$

The error likely to occur in the value of e/m obtained by this method has been discussed by Srivastava (1946) and is about 15%.
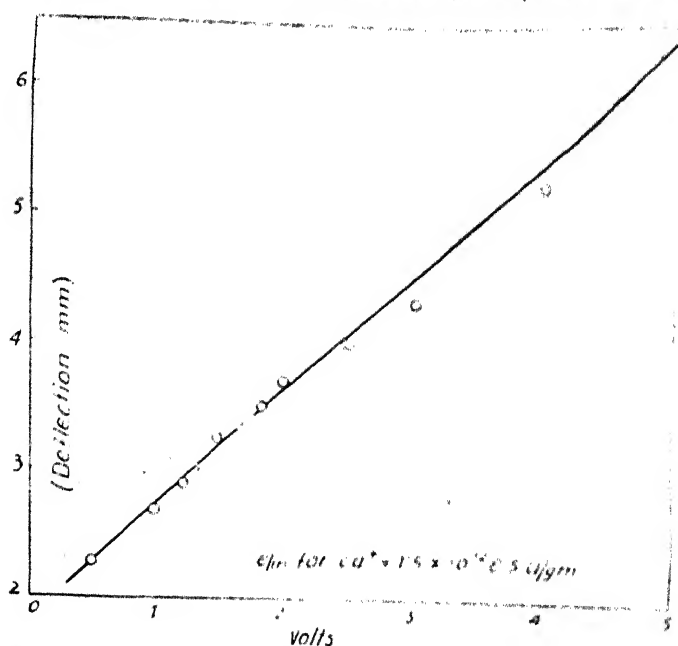

Fig. 1

My best thanks are due to Dr. B. N. Srivastava, D. Sc. under whose guidance the work was done at the University of Allahabad.

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